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**MINING AND ENVIRONMENTAL PROTECTION**

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**PROCEEDINGS**

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## Co/Mo BIMETALLIC CARBIDES WITH POTENTIAL APPLICATIONS AS CATALYST SUPPORT IN PEM FUEL CELLS - SYNTHESIS AND CHARACTERIZATION

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**Abstract:** Co/Mo carbides were prepared by co-impregnation with aqueous solution of metal salts and sucrose into ordered mesoporous SBA-15 silica template using carbothermal hydrogen reduction. The obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS). Electrochemical characterization of obtained materials was performed by cyclic voltammetry in acidic solution. Bimetallic CoMo carbide obtained by using carbothermal hydrogen reduction of Co Mo precursors is formed when the Co/Mo molar ratio is 1.0.

**Key words:** Co/Mo carbides, Co-impregnation, Carbothermal-hydrogen reduction, Cyclic voltammetry, PEM fuel cells

### 1. INTRODUCTION

Alternative power sources such as PEMFCs (proton exchanged membrane fuel cells) commonly use carbon as catalyst support for platinum nanoparticles. Anodic materials of PEMFCs compacted carbon has several disadvantages, electrochemical oxidation leading to agglomeration or even loss of platinum decreasing the catalyst electroactive surface area and consequently lowering the performance of PEMFCs. Therefore, the major challenges in fuel cell research are to reduce the cost of the electrocatalyst either by reduced Pt loading or by developing a non-noble catalyst. Transition metal carbides, typically of group VI, have been reported to have Pt-like chemical reactivity and electronic properties [1–8]. One of the very important advantages of transition metal carbides is that they have a good resistance to very strong catalytic poisons as carbon monoxide, hydrocarbons and hydrogen sulfide [9]. There have been many studies related to the development of transition metal carbides for use as hydrogen fuel cell electrocatalysts. Newsam et al. [10] synthesized  $\text{Co}_6\text{Mo}_6\text{C}_2$  ( $\text{Co}_3\text{Mo}_3\text{C}$ ) by a two-stage reaction method, and the structures of these carbides were firstly confirmed by Rietveld analyses of powder neutron diffraction data [11]. Bussell's group synthesized the bulk and alumina supported  $\text{Co}_3\text{Mo}_3\text{C}$  through a temperature-programmed nitridation and subsequent topotactic carburization route [12]. Xiao et al., used oxide precursor instead of nitride and operated the carburization under the flow of  $\text{C}_2\text{H}_6/\text{H}_2$  mixture [13]. On the other hand, Lang et al. developed a carbothermal hydrogen reduction method for the preparation of Co-Mo carbide [14] as well as nanostructure  $\beta\text{-Mo}_2\text{C}$  [15] and  $\text{W}_2\text{C}$  [16]. Wang and coworkers [9] successfully synthesized two phases of cobalt-molybdenum bimetallic carbides,  $\text{Co}_3\text{Mo}_3\text{C}$  and  $\text{Co}_6\text{Mo}_6\text{C}$ , both prepared by the Hexamethylenetetramine based one-step thermal decomposition method.

In the current study, ordered mesoporous silica (e.g. SBA-15) was used as hard template in the synthesis procedure of cobalt–molybdenum bimetallic carbide. Silica template labeled as SBA-15 (Santa Barbara No. 15) possess relatively large pores and simple pore structure which can be gained in the presence of amphiphilic poly(alkylene oxide)-type triblock copolymers. Mesoporous silica SBA-15 employed as a hard template was infiltrated with aqueous solution of metal salts (Co/Mo) and sucrose (as carbon source) followed by its carbonization, and subsequent template removal in order to obtain Co–Mo carbides. The obtained catalyst support inherited well preserved microstructure and satisfactory electronic conductivity.

## 2. EXPERIMENTAL

### 2.1. Synthesis of Co–Mo carbide

The parent SBA-15 silica template was synthesized according to literature procedure [17]. Commercially available solvents and reagents were used in the whole procedure. Sample referred to as A was synthesized according to following procedure. Mesoporous silica SBA-15 material (0.5 g) was first impregnated with 4.1 ml of  $0.01 \text{ mol L}^{-1}$   $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (Merck) aqueous solution under stirring. The obtained material was dried at  $140^\circ\text{C}$  for 24 h and then crushed to get a fine powder. The resulting material was then impregnated again with 2.8 ml of  $0.01 \text{ mol L}^{-1}$   $(\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (Merck) aqueous solution, under stirring. The obtained material was dried at  $30^\circ\text{C}$  and then at  $50^\circ\text{C}$  for 24 h and then crushed to get a fine powder. The atomic ratio of Co/Mo = 1 was fixed, while the  $(\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  were mixed with a mole ratio of 7:1. Finely, 0.5 g of obtained material was impregnated with aqueous solution obtained by dissolving 0.8 g of sucrose (BDH Prolabo) and 0.1 g of  $\text{H}_2\text{SO}_4$  (p.a., Gontrohem) in  $4 \text{ cm}^3$  of distilled water. The mixtures were heated for 6 h at  $100^\circ\text{C}$  and for 6 h at  $160^\circ\text{C}$ . The material was impregnated again with aqueous solution obtained by dissolving 0.5 g of sucrose, 0.05 g of  $\text{H}_2\text{SO}_4$  and  $2.5 \text{ cm}^3$  of distilled water, the sample was treated for 6 h at  $100^\circ\text{C}$  and for 6 h at  $160^\circ\text{C}$ . Obtained material was heated in a conventional furnace, at  $500^\circ\text{C}$  held for 2h in hydrogen flow, and underwent carbothermal reduction at  $900^\circ\text{C}$  held for 2h in argon flow. After the heat treatment, the samples were cooled to room temperature under argon.

### 2.2. Template removal of SBA-15 replicas

The SBA-15 template was removed by mixing 0.5 g of the obtained powders with  $10 \text{ cm}^3$  of HF (p.a. 40%, Merck) for 20 h and washing in  $200 \text{ cm}^3$  of ethanol and distilled water, until the neutral pH reaction. Obtained powders were dried on air at  $120^\circ\text{C}$  for 24 h.

### 2.3. Characterization methods

X-ray diffraction data were collected on a Philips PW 1050 diffractometer with Cu-K $\alpha$ <sub>1,2</sub> radiation (Ni filter) at the room temperature. Measurements were done in  $2\theta$  range of  $5\text{--}80^\circ$  with a scanning step width of  $0.05^\circ$  and 1s times per step. The morphology of the produced powders was performed using JEOL JCM-5800 LV scanning electron microscope (SEM) covered with thin film of gold for better image definition, while SEM/EDS analysis was performed on the samples with Au/Pd coating by VEGA TS 5130 mm, TESCAN scanning electron microscope. Electrochemical characterization of obtained samples was performed by cyclic voltammetry (CV). All measurements were performed using Gamry electrochemical system in a three electrode configuration consisting of an Au rotating disk electrode (RDE) as the working electrode, a Pt mesh as the counter electrode, and Saturated Calomel Electrode (SCE) as the reference electrode. Catalyst inks were prepared by mixing 0.002 g of samples A and B,  $12.5 \mu\text{L}$  Nafion solution and  $988 \mu\text{L}$  of isopropanol. The mixture is homogenized for 15 to 20 minutes in an ultrasonicator and  $40 \mu\text{L}$  of the mixture was then deposited onto the working electrode surface. CV data was obtained in  $0.5\text{M}$   $\text{HClO}_4$  electrolyte before purging with Nitrogen for 30 minutes to completely remove oxygen.

The potential scan was carried out at rates of 20, 50 and 100 mVs<sup>-1</sup> in the range of -0.6 V to 1.0V. After the scan was stabilized during the first 5-10 cycles, CV curves were recorded. All the CV curves are plotted against the SCE.

### 3. RESULTS AND DISCUSSION

The XRD pattern of as prepared sample referred to as A is shown in Figure 1. The most intense peaks of the A pattern locating at  $2\theta = 43.08, 43.08, 32.8, 35.84$  and  $47.1$  match quite well with standard data of face-centered cubic  $\text{Co}_6\text{Mo}_6\text{C}$  and  $\text{Co}_3\text{Mo}_3\text{C}$  [1], except for a small quantity of  $\text{Mo}_2\text{C}$  and  $\text{Co}_3\text{C}$  impurities, marked as asterisks in the Figure 1a).

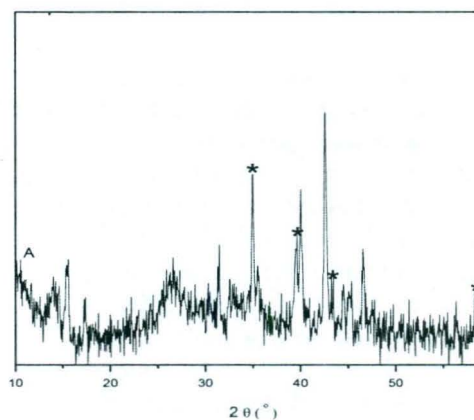


Figure 1. XRD pattern of obtained sample: A.

The SEM micrographs of the SBA-15 template (Figures 2a)) and as-prepared sample referred to as A is shown Figure 2(c). SBA-15 consists of many peanut-like domains with relatively uniform sizes (about 0.5  $\mu\text{m}$ ) which are aggregated into wheat-like structures. According to these images amorphous structure of the samples is evident. The SEM image of the as-prepared sample referred to as A shows that the obtained samples is porous material with structure which is an inverse replica of the SBA-15 template, with irregular particles accumulating on large agglomerates.

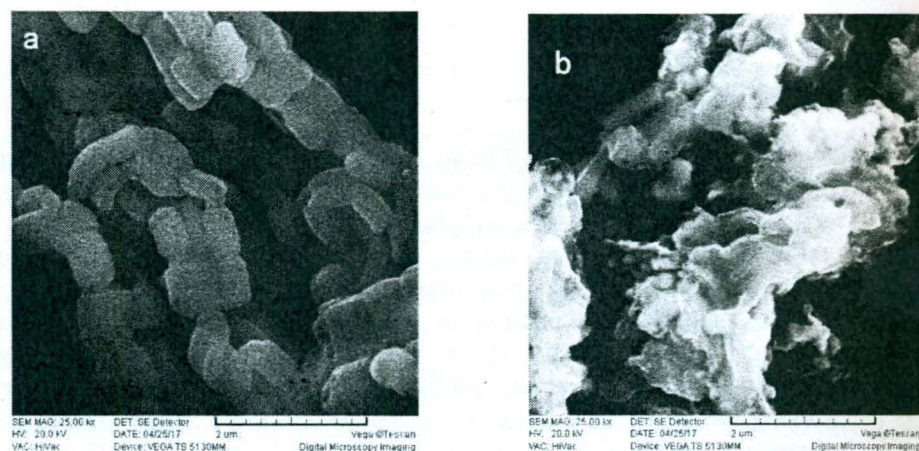


Figure 2. SEM images of the obtained samples: (a) SBA-15 template, and (c) sample A.

Detailed SEM/EDS analysis of the SBA-15 template and as-prepared sample, sintered at 900°C are given in Figure 3. Chemical composition obtained SBA-15 template by EDS analysis of agglomerates, corresponds to the  $\text{SiO}_2$  phase with a trace of Au peaks, due to Au coating of the samples (Site no 1, Figure 3a). Chemical composition obtained by EDS analysis of agglomerates, sample denoted as A (Figure 3b)), corresponds to the result obtained by XRD analysis:  $\text{Co}_6\text{Mo}_6\text{C}$  phase (Site no 1 and Site no 2).

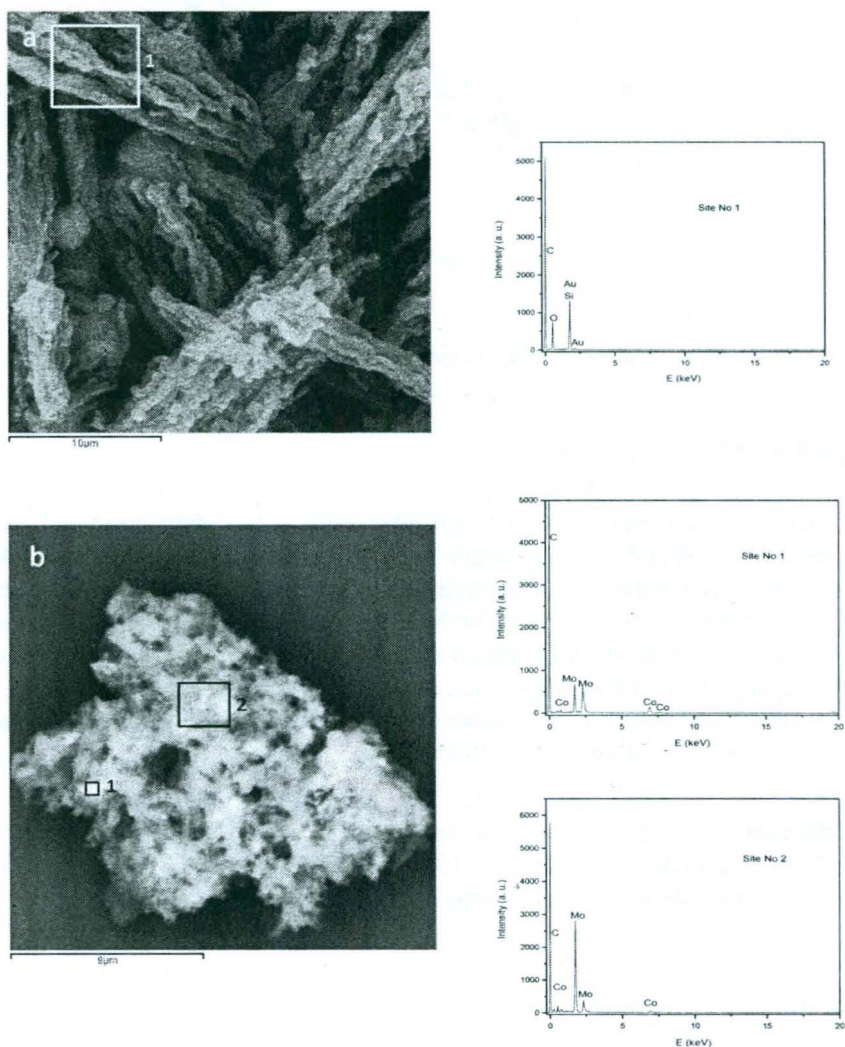
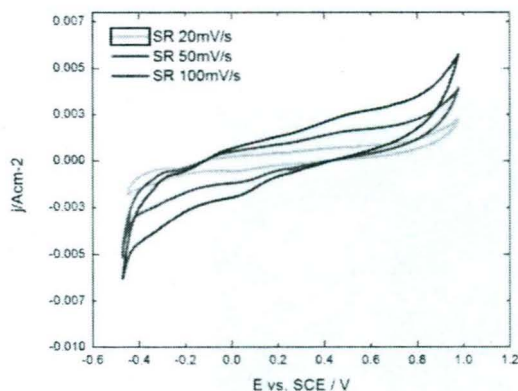


Figure 3. SEM micrographs of obtained samples: (a) SBA-15 template, (b) A.

Cyclic voltammetry on selected sample A was performed in 0.5M  $\text{HClO}_4$  in order to determine the stability in acidic conditions under the potential ranges suitable for operation in PEM fuel cells. Stability window is defined as the potential range in which the investigated catalyst support does not undertake any irreversible change during anodic oxidation and cathodic reduction. The results presented in Figure 4 shows stability of 1.5 V for the sample referred to as A. The cyclic voltammogram in Figure 4 a) for the sample A exhibits pronounced hydrogen UPD (under potential deposition) region. Small peak at about 0 V vs SCE, which could originate from two effects can be seen on cyclic voltammogram. One is possible interaction of the carbides with the adsorbed hydrogen [18,19] and the other is change in the oxidation state of the prepared CoMo carbides. These results indicate that the investigated sample could serve as catalyst support to be applied in PEM fuel cells.



a)

Figure 4. Cyclic voltammograms for (a) sample A obtained in 0.5M HClO<sub>4</sub> electrolyte at different scan rates.

### 3. CONCLUSION

The monometallic and bimetallic CoMo carbides were successfully prepared by co-impregnation into ordered mesoporous SBA-15 silica template with aqueous solution of metal salts and sucrose using carbothermal hydrogen reduction. Bimetallic Co<sub>6</sub>Mo<sub>6</sub>C and Co<sub>3</sub>Mo<sub>3</sub>C, except for a small quantity of Mo<sub>2</sub>C and Co<sub>3</sub>C impurities is obtained. The SEM image of the as-prepared sample showed that the porous materials are obtained with structure which is an inverse replica of the SBA-15 as a template. Chemical composition EDS analysis of agglomerates, corresponds to the result obtained by XRD analysis. Cyclic voltammetry results indicate that investigated sample could serve as catalyst support for PEM fuel cells application, which will be subject of our future work.

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